GROWTH OF EPITAXIAL $BaTiO_3$ THIN FILMS AT 600°C BY METALORGANIC CHEMICAL VAPOR DEPOSITION

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ABSTRACT

Metalorganic chemical vapor deposition (MOCVD) was used to deposit epitaxial $BaTiO_3$ thin films on (100) MgO substrates at 600°C. The metalorganic precursors employed in the deposition experiments were hydrated $Ba(thd)_2$ (thd = $C_{11}H_{19}O_2$) and titanium isopropoxide. The films were analyzed by means of transmittance spectroscopy, wavelength dispersive x-ray spectrometry, secondary ion mass spectrometry depth profiling, x-ray diffraction, high resolution transmission electron microscopy, selected area electron diffraction, nanoscale energy dispersive x-ray spectrometry and second harmonic generation measurements. There was no evidence for interdiffusion between the film and substrate. The x-ray and electron diffraction studies showed that the films were oriented with the **a**-axis normal to the substrate surface, whereas second harmonic generation measurements showed that the films had some **c**-axis character.

INTRODUCTION

The nonlinear optical properties of the ferroelectric oxide $BaTiO_3$ make this material a potential candidate for electro-optic modulators and switches,[1] optical memory and optical processing devices,[2] and frequency doublers.[3] Production of such devices requires the development of a commercially feasible technique for depositing epitaxial $BaTiO_3$ thin films. MOCVD is generally recognized as a technique with great potential for scale-up to production levels. Several groups have reported on epitaxial $BaTiO_3$ thin films grown by MOCVD.[4-8] In this paper, we describe the *in situ* growth of epitaxial $BaTiO_3$ films by thermal MOCVD on (100) MgO substrates at 600°C. This temperature is 200°C or more lower than the temperatures reported for the growth of epitaxial $BaTiO_3$ thin films by other thermal MOCVD processes[4-6,8] and 80°C lower than the temperature reported for growth by a plasma-enhanced MOCVD process.[7] It is desirable to use a low substrate temperature for several reasons. Lower substrate temperatures result in less interdiffusion between the film and substrate and smaller concentrations of undesirable thermally activated defects. In addition, lower substrate temperatures are more compatible with silicon integrated circuit processing where the diffusion of dopants in the Si-based devices must be minimized.[9]

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EXPERIMENTAL DETAILS

The films were deposited in an MOCVD system described in more detail elsewhere.[10,11] The precursors, titanium isopropoxide [TIP] and bis(2,2,6,6-tetramethyl-3,5-heptanedionato) barium hydrate [$Ba(thd)_2$], were contained in stainless steel bubblers. Dried argon (99.997% pure) was the carrier gas and oxygen (99.5% pure) was the oxidizing gas. A set of conditions for epitaxial growth is presented in Table I. In order to prevent condensation of $Ba(thd)_2$, all gas lines downstream of the $Ba(thd)_2$ bubbler were maintained at 240°C (10°C above the bubbler temperature). The cleaved (100) MgO substrate (dimensions 13 mm x 13 mm x 0.5 mm) was supported on a SiC-coated graphite susceptor. The susceptor was positioned in the center of a horizontal quartz reactor tube and heated by a radio frequency induction generator. An ungrounded, sheathed thermocouple was used to measure the temperature in the center of the susceptor about 1.5 cm from the backside of the substrate. A temperature reading of 560°C for this thermocouple corresponded to a substrate surface temperature of 600°C as measured with a dual wavelength pyrometer.

Two epitaxial films designated BT-64 and BT-67 were examined in the present study. Transmittance spectroscopy[12] measurements were made to estimate the thickness at the center of each film. The $Ba(thd)_2$ precursor was known to contain Sr,[13] and the concentration of Sr in the films was analyzed in an electron microprobe by wavelength dispersive x-ray spectrometry. Secondary ion mass spectrometry (SIMS) depth profiling measurements were conducted to assess the compositional uniformity through the thickness of the films. The epitaxial nature of the films was studied by x-ray diffraction, high resolution transmission electron microscopy (HRTEM), and selected area electron diffraction techniques. Interdiffusion between the film and substrate was investigated by SIMS depth profiling measurements and by energy dispersive x-ray spectrometry measurements in a TEM using a probe diameter of 2-3 nm. Second harmonic generation (SHG) measurements as a function of angle of incidence were performed with p-polarized fundamental (1.06 μm wavelength from a pulsed Nd:YAG laser) and second harmonic beams in a system calibrated with a quartz single crystal. For single domain, tetragonal $BaTiO_3$ in this geometry, a minimum in the SHG vs. angle of incidence is expected when the light propagates along the c-axis.

TABLE I. $BaTiO_3$ Growth Conditions

Substrate	MgO (100)
Substrate temperature (°C)	600 ± 3[a]
Reactor pressure (kPa[b])	6.67 ± 0.01
Temperature of $Ba(thd)_2$ (°C)	230 ± 1
Temperature of TIP (°C)	25 ± 1
Flowrate of Ar through $Ba(thd)_2$ (sccm)	75.0 ± 0.1
Flowrate of Ar through TIP (sccm)	70.0 ± 0.1
Oxygen gas flowrate (sccm)	300.0 ± 0.1
Pressure over TIP (kPa[b])	37.30 ± 0.01
Deposition time (h)	3.0

[a] The uncertainty given for a variable indicates the observed fluctuation in the value during a deposition experiment.

[b] 1 kPa = 7.5 Torr.

RESULTS AND DISCUSSION

The films were transparent and displayed color fringes indicative of variations in film thickness. The thicknesses at the centers of films BT-64 and BT-67 were 570 and 500 nm, and the corresponding growth rates were 190 and 170 nm/h. Films BT-64 and BT-67 had Sr concentrations of 0.3 and 1.0 atomic percent respectively. At these low concentrations, the changes in the **a** and **c** lattice parameters of tetragonal $BaTiO_3$ due to Sr were calculated to be less than 0.002 Å (0.05%).[14] SIMS measurements showed that the composition was uniform through the thickness of the films. There were abrupt changes in the concentrations of Mg, Ba and Ti at the film/substrate interface, indicating minimal interdiffusion.

A conventional x-ray diffraction pattern for film BT-67 is shown in Fig. 1. Only peaks corresponding to the 200 reflection of MgO and the 100, 200 and 300 reflections of $BaTiO_3$ were observed, indicating that the film was highly oriented. The average parameter determined from the three $BaTiO_3$ peaks was 4.000 $\pm$ 0.005 Å. This value is in good agreement with the **a** = 3.994 Å parameter for bulk tetragonal $BaTiO_3$, indicating that the film was oriented with an **a**-axis normal to the substrate surface.

High resolution electron micrographs of film BT-67 showing the film/substrate interface are presented in Fig. 2. The {200} lattice planes are continuous across the interface, demonstrating that the film is epitaxial. These images also show that the film/substrate interface is sharp and contains no second phase. Energy dispersive x-ray spectrometry measurements near the interface showed that the concentration of Mg in the $BaTiO_3$ film and

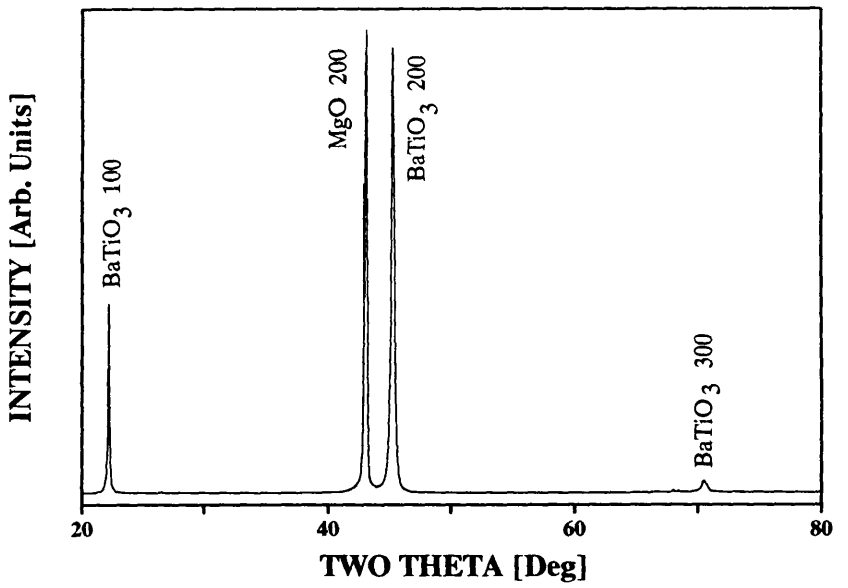

Fig. 1. Conventional x-ray diffraction pattern of film BT-67. Theta was intentionally offset by 0.6° in order to reduce the intensity of the strong MgO 200 reflection and thereby improve resolution of the low angle side of the $BaTiO_3$ 200 reflection.

the concentrations of Ba and Ti in the MgO substrate were below the detectability limit of 2 wt %, indicating that interdiffusion was low.

Misfit dislocations in the $BaTiO_3$ film were observed along the interface (e.g., see arrow in Fig. 2a.) Formation of the dislocations probably occurred during deposition in order to accommodate the 5.4 % lattice mismatch between the substrate and the growing film at the growth temperature; about one misfit dislocation per nine unit cells was needed to fully relieve this mismatch strain. A Burgers circuit analysis[15] of a lattice image gave a measured dislocation frequency of about one per fifteen unit cells.

A selected area electron diffraction pattern of film BT-67 covering a 0.6 μm diameter area of the film and substrate is shown in Fig. 3. The patterns show a "cube-cube" orientation relationship between the $BaTiO_3$ and MgO (i.e., alignment of both the normal and in-plane lattice vectors of the film with those of the substrate), thus confirming that the film is epitaxial. Some arcing of the higher order $BaTiO_3$ diffraction spots was observed, indicating that different regions of the film were slightly misoriented relative to the $<100>$ directions in the MgO substrate. An upper limit of $\pm$ 1° for the misorientation angle was estimated from the extent of arcing. Lattice parameters calculated from the pattern confirmed that the film was oriented with an **a**-axis perpendicular to the substrate surface.

A plot of SHG vs. angle of incidence for film BT-64 is shown in Fig. 4. The minimum at normal incidence (0°) corresponds to $BaTiO_3$ with the **c**-axis normal to the substrate surface, although the film was found to be predominantly **a**-axis oriented from x-ray and electron diffraction measurements. These results suggest that a portion of the film was **c**-axis oriented,

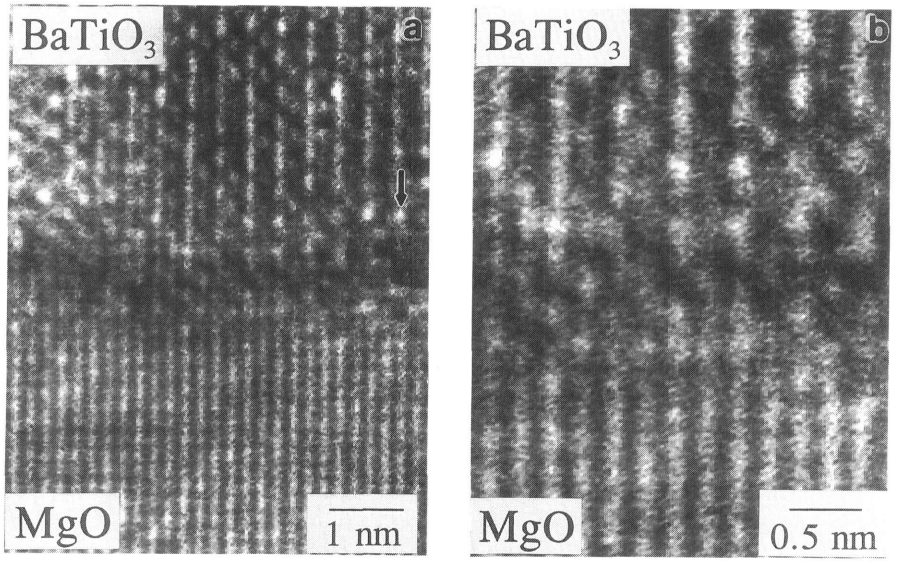

Fig. 2. a,b) High resolution electron micrographs of the film/substrate interface in film BT-67 at two magnifications. The epitaxial nature of the film is clearly evident by sighting down the {200} planes (i.e., the lighter contrast vertical columns) at an oblique angle. A misfit dislocation in the film is indicated by the arrow in micrograph (a).

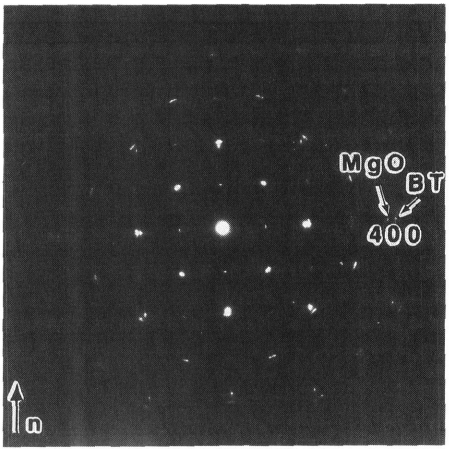

Fig. 3. Selected area electron diffraction pattern of film BT-67 showing the "cube-cube" orientation relationship between the film and the substrate. The arrow indicates the direction of the normal (**n**) to the film/substrate interface.

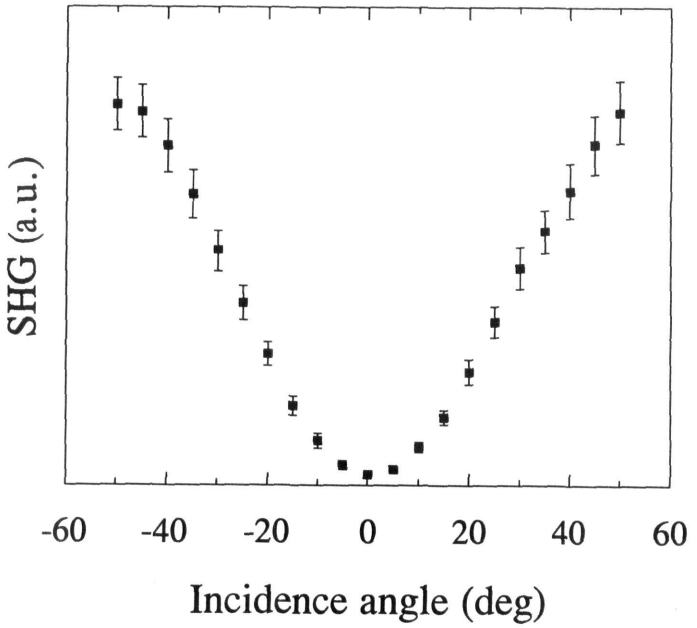

Fig. 4. Second harmonic generation in film BT-64 vs. angle of incidence for p-polarized fundamental and second harmonic beams. The negligible signal for light incident perpendicular to the film plane indicates a portion of the film is c-axis oriented, and this portion dominates the SHG. The error bars are one standard deviation of the set of SHG measurements at a given angle.

and that this portion dominated the SHG. The SHG from film BT-67 was roughly 30 times smaller than from film BT-64, but also suggested a **c**-axis orientation. Since the two films have similiar microstructures, the difference in the SHG may result from a difference in the domain size or the fraction of poled, **c**-axis oriented material in each film. Poling experiments are underway to clarify the difference in the SHG between the two films and to resolve the discrepancy between the orientations obtained from the SHG and diffraction measurements.

CONCLUSIONS

In summary, epitaxial $BaTiO_3$ thin films were grown in-situ on (100) MgO substrates by MOCVD at 600°C. This substrate temperature is the lowest reported temperature for the growth of epitaxial $BaTiO_3$ by an MOCVD process. X-ray diffraction, high resolution electron microscopy, and selected area electron diffraction measurements showed that the films were epitaxial and were oriented with an **a**-axis normal to the substrate surface. Second harmonic generation measurements suggested that the films had some **c**-axis character as well, which is being investigated through poling studies.

References

1. A. M. Glass, Mater. Res. Bull. **XIII** (8), 16 (1988).
2. See e.g., Chapters 10 and 11 in P. Yeh, Introduction to Photorefractive Nonlinear Optics (Wiley, New York, 1993).
3. J. A. Armstrong, B. Bloemberger, J. Ducuing, and P. S. Persham, Phys. Rev. **127**, 1918 (1962).
4. H. Nakazawa, H. Yamane, and T. Hirai, Jpn. J. Appl. Phys. **30**, 2200 (1991).
5. L. A. Wills, B. W. Wessels, D. S. Richeson, and T. J. Marks, Appl. Phys. Lett. **60**, 41 (1992).
6. P. C. Van Buskirk, R. Gardiner, P. S. Kirlin, and S. Nutt, J. Mater. Res. **7**, 542 (1992).
7. C. S. Chern, J. Zhao, L. Luo, P. Lu, Y. Q. Li, P. Norris, B. Kear, F. Cosandey, C. J. Maggiore, B. Gallois, and B. J. Wilkens, Appl. Phys. Lett. **60**, 1144 (1992).
8. P. C. Van Buskirk, G. T. Stauf, R. Gardiner, P. S. Kirlin, B. Bihari, and J. Kumar, in Ferroelectric Thin Films III, edited by B. A. Tuttle, E. R. Myers, S. B. Desu, and P. K. Larsen (Mater. Res. Soc. Proc. **310**, Pittsburgh, PA, 1993), pp. 119-124.
9. S. Wolf and R. N. Tauber, Silicon Processing for the VLSI Era, vol. 1 (Lattice Press, Sunset Beach, CA, 1986), p. 57.
10. D. L. Kaiser, M. D. Vaudin, G. Gillen, C.-S. Hwang, L. H. Robins, and L. D. Rotter, J. Crystal Growth **137**, 136 (1994).
11. D. L. Kaiser, M. D. Vaudin, G. Gillen, C.-S. Hwang, L. H. Robins, and L. D. Rotter, in Metal-Organic Chemical Vapor Deposition of Electronic Ceramics, edited by S. B. Desu, D. B. Beach, B. W. Wessels, and S. Gokoglu (Mater. Res. Soc. Proc. **335**, Pittsburgh, PA, 1994), pp. 47-52.
12. R. Swanepoel, J. Phys. E: Sci. Instrum. **16**, 1214 (1983).
13. Private Communication, Frank Wagner, Strem Chemicals, Inc.
14. D. F. Rushman, and M. A. Strivens, Faraday Soc. Trans. **42A**, 231 (1946).
15. R. E. Reed-Hill, Physical Metallurgy Principles, Second Edition (D. Van Nostrand Co., New York, NY, 1973), pp. 157-158.